SYNTHESIS OF ALUMINUM TITANATE USING STABILIZING ADDITIVES

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The advantages of joint preliminary grinding of the initial-material components, as compared to separate grinding, and its effect on the regularities of phase formation in the aluminum oxide — titanium oxide system are considered. Joint activation makes it possible to shorten the time expended on thermal synthesis of $TiO_2 \cdot Al_2O_3$. The effect of stabilizing additives of magnesium and silicon oxides and talc on the kinetics of thermal synthesis of aluminum titanate is studied. It is proposed that talc in an amount of 7% be used as a stabilizing additive to prevent incongruent melting of $TiO_2 \cdot Al_2O_3$ accompanied by formation of the initial components.

A distinguishing feature of ceramics based on aluminum titanate is the low thermal coefficient of linear expansion of articles made on its basis. Due to that property, it is expedient to use aluminum titanate in nonstationary processes as a material that is resistant to thermal shock. It is used in engines as a heat-insulating material, in crucibles for melting and casting metal in ferrous and nonferrous metallurgy [1], and in catalyst carriers.

Aluminum titanate is produced by firing TiO_2 and Al_2O_3 at a temperature $\geq 1400°C$. However, a drawback of this material consists in its incongruent melting within the temperature interval of 900 – 1250°C with formation of the initial components. Moreover, aluminum titanate has strong anisotropy of thermal expansion, which results in the appearance of numerous microcracks and low strength of sintered products. In order to eliminate these phenomena, SiO_2, MgO, ZrO_2, Y_2O_3, La_2O_3, and other oxides of rare-earth elements are introduced into the system [2].

The depth of the interaction between the oxide-mixture components depends on many factors: the dispersion of the oxides, their origin, the ratio between the mixture components, the compression density, the composition of the ambient medium, and the calcination temperature [3]. One of the ways of intensifying the thermal-synthesis process is preliminary joint dispersion of the initial components and use of hydrated oxides as the raw material [4 – 6]. This paper is devoted to the study of the effect of mechanochemical activation of the initial material and stabilizing additives on the synthesis of aluminum titanate.

The initial material was the intermediate product of the hydrosulfuric acid method for production of titanium dioxide, which consisted of TiO_2 (anatase) — 26.2%, $TiO_2 \cdot H_2O$ (metatitanic acid) — 61.0%, and $TiO_2 \cdot SO_3 \cdot H_2O$ (basic titanium sulfate) — 12.8% (here and elsewhere the mass content is indicated unless otherwise specified). Since $TiO_2 \cdot H_2O$ is the main phase of this raw material, hereafter it will be called metatitanic acid. After heat treatment of the titanium-containing material for 6 h at a temperature of 450°C, the metatitanic acid is dehydrated, TiO_2 (anatase) is the prevailing phase (85.6%), and the content of $TiO_2 \cdot SiO_3 \cdot H_2O$ is 14.4%.

Aluminum oxide was introduced in the form of either $Al_2O_3 \cdot 3H_2O$ (~ 100% hydrargillite) or G-00 alumina (the $\alpha\text{-}Al_2O_3$ content is 50 – 60%, and the rest is $\gamma\text{-}Al_2O_3$). The molar ratio of $TiO_2 : Al_2O_3$ in all mixtures was 1 : 1.

The stabilizing additives that prevented incongruent melting of aluminum titanate and formation of the initial oxides were MgO, SiO_2, and talc ($3MgO \cdot 4SiO_2 \cdot H_2O$) in an amount of 5%.

Grinding and mechanical activation of the initial components and their mixtures were performed in a VM-4 roll-circular vibration mill (electric intensity 5.4 kW/kg). The stoichiometric mixtures with stabilizing additives were calcined at a temperature of 1400°C. The calcination duration varied.

X-ray phase analysis was carried out on a DRON-3M diffractometer (CuK_α radiation). The crystallographic phases were identified by correlation with data supplied in [7].

To synthesize aluminum titanate, two systems were selected, one of which consisted of a mixture of oxides, and the other was a mixture of hydrated titanium and aluminum oxides.

After joint activation of the initial components in a vibration mill for 1 h, no new crystallographic phases were identi-

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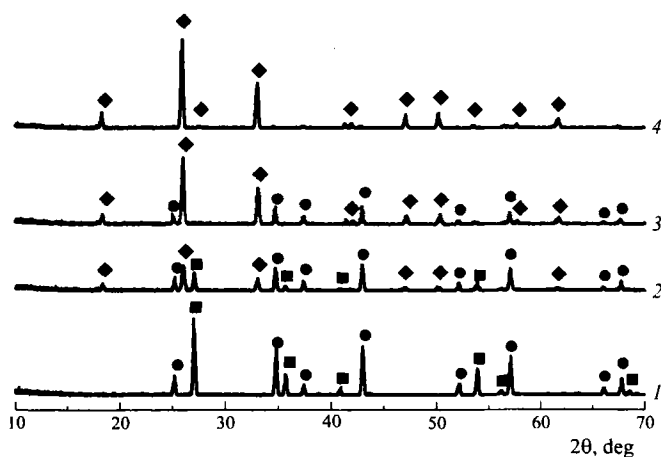[1] Ivanovo State Chemical Engineering University, Ivanovo, Russia.

Fig. 1. Diffraction patterns (CuK$_\alpha$ radiation) of samples based on compositions of Al(OH)$_3$ - TiO$_2$ · H$_2$O (molar ratio of TiO$_2$: Al$_2$O$_3$ = 1 : 1) after joint preliminary activation of the components and calcination at a temperature of 1400°C: *1*) without additive, calcination duration 180 min; *2*) 5% talc, calcination duration 15 min; *3*) 7% MgO, calcination duration 60 min; *4*) 7% talc, calcination duration 60 min; ◆) TiO$_2$ · Al$_2$O$_3$; ●) α-Al$_2$O$_3$; ■) TiO$_2$ (rutile).

Fig. 3. Effect of the amount of stabilizing talc additive on the degree of conversion of aluminum titanate calcined for 60 min at a temperature of 1400°C. Material: Al(OH)$_3$, TiO$_2$ · H$_2$O (molar ratio 1 : 1); joint preliminary mechanical activation of the components.

fied, and only partial amorphization of the initial components was observed. The changes in the parameters of the titanium dioxide substructure as a function of the duration of grinding in a vibration mill together with aluminum oxide and hydroxide had been investigated by us earlier [8].

An x-ray phase analysis of initial samples calcined for 3 h at a temperature of 1400°C without stabilizing additives revealed that after both joint and separate preliminary dispersion of the material the system consisted of just a mechanical mixture of high-temperature oxides of titanium (rutile) and aluminum (α-Al$_2$O$_3$). The phase of aluminum titanate was not identified in this case (Fig. 1). This is evidence of the fact that aluminum titanate decomposes into the initial components at high temperatures.

The kinetics of aluminum titanate formation was calculated from the change in the integral intensity of the reflec-
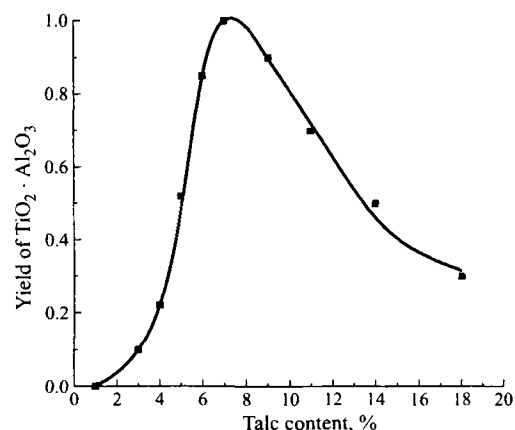
tion from the plane of 3.345 Å. The stabilizing additive that impeded incongruent melting of TiO$_2$ · Al$_2$O$_3$ was 5% talc. The change in the integral intensity of the peak of aluminum titanate as a function of the calcination duration had an S-shaped character in all samples (Fig. 2), which is typical of topochemical reactions.

The investigation included selection of a topochemical model to describe the process of aluminum titanate synthesis. Calculations carried out on different kinetic models indicated that the process of thermal synthesis of aluminum titanate is described with the highest accuracy by the Avraami – Erofeev equation, which in integral form is as follows [3, 9]:

$$k\tau = (-\ln{(1 - \alpha)})^n,$$

where k is the observed rate constant of the process; τ is the time; α is the degree of transformation; $n = 1/3$ is a constant that depends on the nature of the crystal nucleation and growth processes ($n = \beta + \lambda$, where β is the number of stages

TABLE 1

Sample	Initial-material composition	Stabilizing additive	Activation	Phase composition of samples after calcination*			Observed rate constant in Avraami – Erofeev equation $k \times 10^4$, sec^{-1}
				TiO$_2$ · Al$_2$O$_3$	α-Al$_2$O$_3$	TiO$_2$ (rutile)	
1	Al$_2$O$_3$ · 3H$_2$O, TiO$_2$ · H$_2$O	5% talc	Joint	+(0.60)	+(0.22)	+(0.18)	0.86
2	The same	The same	Separate	+(0.09)	+(0.51)	+(0.40)	0.09
3	Al$_2$O$_3$, TiO$_2$	"	Joint	+(0.18)	+(0.46)	+(0.36)	0.19
4	The same	"	Separate	+(0.05)	+(0.53)	+(0.42)	0.04
5	Al$_2$O$_3$ · 3H$_2$O, TiO$_2$ · H$_2$O	3% talc	Joint	+(0.12)	+(0.49)	+(0.39)	0.12
6	The same	7% talc	The same	+(1)	–	–	4.80
7	"	9% talc	"	+(0.88)	+(0.07)	+(0.05)	1.96
8	"	7% MgO	"	+(0.72)	+(0.16)	+(0.12)	1.19
9	"	7% SiO$_2$	"	–	+(0.56)	+(0.44)	0.02

* Figures in parentheses indicate the relative integral intensity of diffraction peaks.
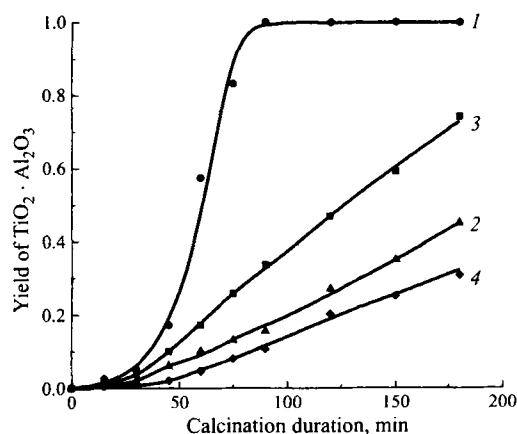
Fig. 2. Kinetic curves of aluminum titanate formation in various initial compositions at a temperature of 1400°C in the presence of 5% talc (molar ratio of $TiO_2 : Al_2O_3$ in all samples 1 : 1): $1, 2$) $Al(OH)_3$, $TiO_2 \cdot H_2O$; $3, 4$) Al_2O_3, TiO_3; preliminary mechanical activation of the components: $1, 3$) joint activation; $2, 4$) separate.

Fig. 4. Kinetic curves of aluminum titanate formation in compositions of $Al(OH)_3$ and $TiO_2 \cdot H_2O$ (molar ratio 1 : 1) subjected to joint preliminary mechanical activation at a temperature of 1400°C: 1) 7% talc; 2) 7% MgO; 3) 7% SiO_2.

in nucleus formation, λ is the number of directions of effective nucleus growth).

Based on this equation, the reaction rate constants were determined, which are given in Table 1. The composition and characteristics of samples based on equimolar compositions of $TiO_2 - Al_2O_3$ and $TiO_2 \cdot H_2O - Al_2O_3 \cdot 3H_2O$ calcined for 60 min at a temperature of 1400°C are also given in Table 1.

The positive effect of joint activation of the initial components on the thermal synthesis of aluminum titanate is obvious (see Fig. 2 and Table 1). For systems with a 5% talc additive, the highest rate of aluminum titanate formation is exhibited by a mixture that consists of hydrated aluminum and titanium oxides and is subjected to joint grinding. In this case after 15 min of calcination at a temperature of 1400°C, in addition to diffraction peaks corresponding to titanium and aluminum oxides, intense reflections appear that in being matched to the catalog [7] make it possible to speak of the appearance of aluminum titanate in the system (see Fig. 1, diffraction pattern 2, and Fig. 2). Heat treatment of this composition for 90 min ensures virtually complete formation of $TiO_2 \cdot Al_2O_3$.

After separate preliminary activation of the initial components even three-hour calcination does not provide complete conversion, and reflections related to α-Al_2O_3 and rutile can be identified on the diffraction patterns (see Fig. 2 and Table 1). It is probable that in joint activation the initial components are mixed at the level of clusters and form aggregates of finely disperse powders. Therefore, after joint preliminary dispersion of the components, the thermal-synthesis process is accelerated compared to separate grinding. Thus, joint preliminary activation of the system has a positive effect on the rate and completeness of thermal synthesis of aluminum titanate.

Similar phenomena can be observed in the production of $TiO_2 \cdot Al_2O_3$ from oxides. However, in this case the weight

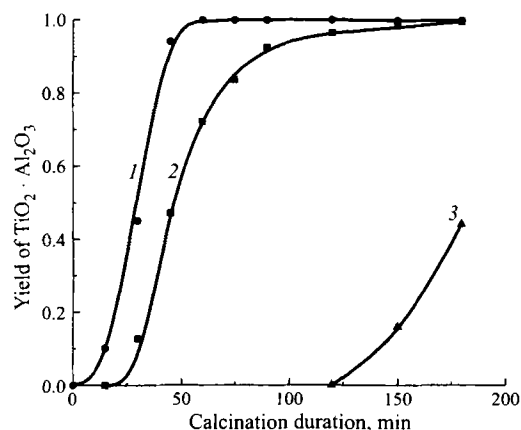fraction of aluminum titanate in the mixture after the same duration of the process is lower than when hydrated oxides are used (see Fig. 2). This can be accounted for by the fact that in order to accelerate the rate of interaction between the reactant particles, the area of the surface of their contact (in other words, their dispersion) should be increased. Hydroxides (hydrargillite, in particular) have a laminar structure, and in joint activation of the initial components, intercollation is observed, i.e., incorporation of atoms and ions of one element in the crystal lattice of another element, and as a consequence, precursor structures (nuclei) of the final product appear.

Thus, intercollation substantially facilitates the process of thermal synthesis of aluminum titanate. This is supported by the kinetic curves of $TiO_2 \cdot Al_2O_3$ formation (see Fig. 2). In using hydrated oxides and joint mechanical activation, the induction period of the beginning of the topochemical reaction is shortened. Moreover, in the case of using hydrated oxides, the mechanical-activation efficiency is significantly higher than in the case of mixing anhydrous oxides. This is due to the high mobility of the proton in the OH group and its capacity for forming hydrogen bonds and facilitating the rupture of other bonds [10], i.e., the mechanochemical activation proceeds under "mild" conditions [11]

On this assumption, further experiments were performed using a system consisting of hydrated aluminum and titanium oxides that was subjected to joint grinding for 60 min.

Let us consider the effect of the amount of stabilizing talc additive on thermal synthesis of aluminum titanate. It is seen from Fig. 3 that the maximum yield of $TiO_2 \cdot Al_2O_3$ is observed in the case where the talc additive amounts to around 7%. In this case, after calcination for 60 min at 1400°C the initial components completely convert to aluminum titanate (see Fig. 1, diffraction pattern 4, and Fig. 3). A further increase in the content of this stabilizing additive in the mixture prolongs the time expended for aluminum titan-

ate synthesis. Introduction of over 20% magnesium silicate is undesirable for toxicological reasons.

In the present study, besides talc, magnesium amd silicon oxides were used as stabilizing additives. As can be seen in Fig. 4 and Table 1, aluminum titanate synthesis proceeds at the highest rate when 7% talc is used as the stabilizing additive. Moreover, it is established that similarly to the use of talc, the optimum quantity of magnesium and silicon oxides is 7%. However, in using these oxides the rate of $TiO_2 \cdot Al_2O_3$ formation is somewhat lower, and after the same calcination period the diffraction patterns in the first case exhibited, apart from aluminum titanate, the phases of titanium and aluminum oxides (see Fig. 1, diffraction pattern 3, and Table 1), and in the second case synthesis of aluminum titanate started only after 120 min of calcination (see Fig. 4). Therefore, of all the suggested additives talc is the most effective. The results obtained in this study agree well with the data in [12], where zirconium compounds were used as stabilizing additives.

Thus, the present study demonstrates the advantages of joint preliminary activation of the system components, as compared to separate activation. Joint activation makes it possible to reduce the time needed for thermal synthesis of $TiO_2 \cdot Al_2O_3$.

It is found that hydrated aluminum and titanium oxides are the most suitable initial materials for aluminum titanate synthesis. In this case the mechanochemical interaction proceeds under "mild" conditions, which subsequently has a positive effect on the rate and completion of thermal synthesis of aluminum titanate. The yield of aluminum titanate increases (compared to a system consisting of nonhydrated oxides) for the same duration of the process.

It is suggested that talc in an amount of 7% be used as a stabilizing additive to prevent incongruent melting of $TiO_2 \cdot Al_2O_3$ accompanied by formation of the initial components.

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